THE SPECTRO-CHEMICAL ANALYSIS OF FERROUS ALLOYS WITH THE MEDIUM QUARTZ SPECTROGRAPH

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ABSTRACT. A preliminary report is given of the spectro-chemical determination of the elements Al, W, V, Mo, Ni, Cr, Cu, Mn and Si found in the ferrous alloys by means of the medium spectrograph. This instrument is not considered to be good enough for this work on account of its low dispersion The calibration curve obtained for the above elements are given. The curves are regular and smooth, showing that the instrument can possibly be used for carrying out the ferrous alloys analysis.

INTRODUCTORY

The spectro-chemical analysis of the ferrous-alloys is carried out by means of Hilger large quartz Littrow spectrograph or its equivalents of other makes. Iron having a large number of lines the separation of them from one another or from those of the alloying or the impurity elements is only possible by a prism spectrograph of the large Littrow type or a good grating instrument. This has been the custom for the analysis of the ferrous alloys till now. In our attempt to determine quantitatively the aluminium traces occurring in the ferrous alloys, some difficulties in exciting the spectral lines of Al were experienced. It should be mentioned that the importance of the presence of the small traces of Al in controlling the grain of the Fe-alloys is just being realised. The chemical determination of the Al-traces is rather difficult specially in the presence of some of the alloying elements. It has thus become necessary to explore the possibilities of the spectro-chemical determinations of the Al-traces present in the ferrous-alloys. The percentage of the Al present is much less than 0.1 per cent. varying generally in the neighbourhood of 0.005 per cent. or less. The simple condensed spark method of excitation of the Fe spectrum is not sufficiently strong to bring out the Al-lines from such small percentages. The high voltage A. C. arc or some special types of the condensed spark have been found necessary by the workers in different countries to make the Al-lines appear with sufficient intensities for the photometric work. The partial success realized by these workers is mostly due to the special devices employed for exciting the spectra. In view of the want of these special devices at present in our laboratory we have tried to photograph the spectra with the medium quartz spectrograph and the simple spark method of excitation available. The Al-lines should not only be excited but should also be sufficiently separated from

all possible interfering lines so as to make the photometric observations of their blackenings reliable. Fortunately it has been possible to satisfy both of these conditions in the present investigation and the Al-contents as low as 0.005 per cent. have accurately been determined. It has not been possible to collect or prepare the standard samples from the steel made in the Works and get their contents chemically and accurately determined. Standard samples have been then prepared synthetically by dissolving spectroscopically pure iron in HCl and then converting it into $FeCl_3$ with HNO_3. Measured amounts of Al of the same quality dissolved in HCl mixed with HNO_3 have been then added to the Fe-solutions. Steps have been taken to keep the solutions just a little acidic. Standard solutions with Al-contents 0.005, 0.01, 0.02, 0.03, 0.05, 0.075, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.50% have in this way been prepared.

EXPERIMENTAL

Hilger medium quartz spectrograph has been used for photographing the spectra. The following are the conditions for excitations:—

Voltage	...	...	8,000 volts.
Capacity	...	...	0.005 μF.
Inductance	...	...	0.25 μH.
Spark gap	...	...	2.0 mm.
Upper electrodes	...	...	Pointed carbon rods.
Lower electrodes	...	...	Graphite rod formed into a cup at the top.

Drillings of the samples to be analysed have been dissolved in HCl and HNO_3 and dried. They have again been dissolved in H_2O and HCl and filtered. The residue has then been ignited and fused with $KHSO_4$, dissolved in H_2O mixed with HCl and added to the original solution. A proportionate amount of $KHSO_4$ has also been added to the standard solutions for making the conditions uniform. Care has been taken to keep the iron and the acid contents of both types of solutions approximately the same. A few drops of these solutions have been taken into the cups formed on the upper end of the lower electrodes and dried by slow heating. For very low percentages of Al a large number of drops is necessary for making the Al-lines sufficiently intense. Only 0.5 minutes pre-sparking has been given to the electrodes and the exposure has been of one minute's duration. The Al-lines 3082.16 and 3961.53 appear clearly on the plates and it has been possible to measure their blackening with photometer. Occasionally the 3092.72 line has also been used for extremely low percentages. But the line 3082.16 is found to give more consistent results. The attached calibration curve (figure 1) is seen to

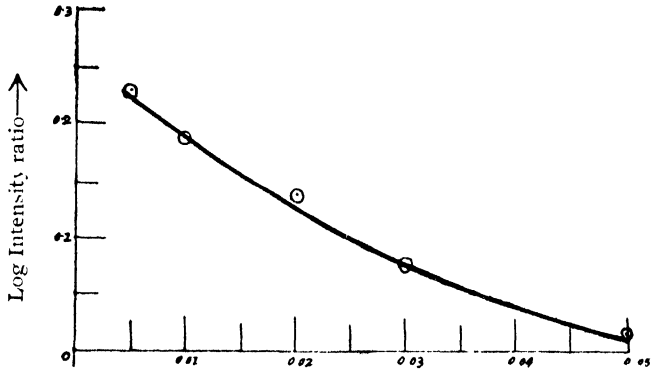


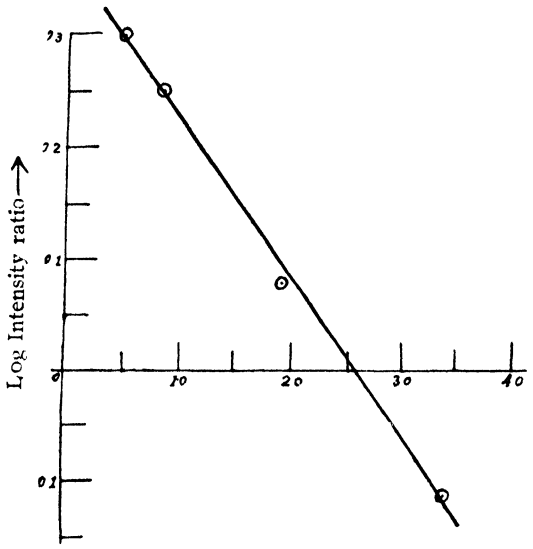
FIG. 1

be very smooth and regular. The agreement with the chemical determinations is satisfactory, but sometime the results differ considerably, the chemical methods yielding higher values. The spectrum of the Al-ppt. obtained by the phosphate method during the chemical determinations has been found to contain the lines of Fe, Mg and Si besides those of Al. The impurity lines are fairly heavy; the higher values obtained chemically may thus be due to the presence of the above elements in the precipitate.

The spectrochemical determinations of W, V, Mo, Ni, Cr, Cu, Mn and Si in the ferrous alloys:—

The successful determination of the Al-traces in the ferrous alloys by the medium quartz spectrograph obviously suggests the possibilities of the spectro-chemical evaluation of the percentages of the above elements as well by the same apparatus. It has also been necessary to try to determine the W-contents by a smaller and more sensitive instruments than the large quartz spectrograph. The simple sparking arrangement at our disposal is not sufficiently powerful for the determination of tungsten less than 2% or so by the large instrument. A prolonged exposure, though brings out the W-line for 0.5% produces so much fogging that the photometric work becomes difficult. The line, 4008.8Å which is generally used for the spectro-chemical work lie in the region where the ordinary plates just begin to be insensitive. The use of the panchromatic plate may ease the situation to a certain extent but that will be an additional complication introduced in the process. The medium quartz spectrograph has, therefore, been tried and the line 2307.1Å of the ionized tungsten appears on the plate even with such lower voltage and an inductance of 0.13 μH in the circuit. The blackening produced by the line is sufficiently strong for the photometric work and for a tungsten content as low as 0.50%. Fig. 2 given below for tungsten shows that the readings are very consistent.

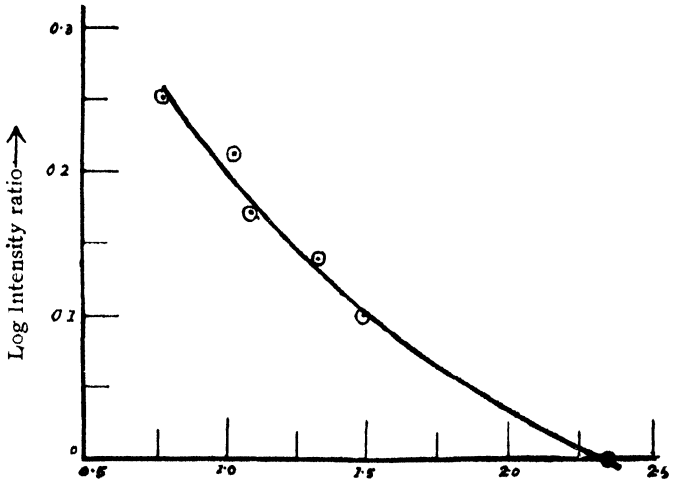
A general search has then been made for suitable lines belonging to the rest of the elements used in the steel making. As mentioned previously the medium spectrograph is not considered to be just the apparatus for the



Percentage of W

FIG. 2

spectro-chemical analysis of the ferrous alloys on account of the crowding for the lines not only belonging to the iron spectrum but also to those of the rest of the elements present in the sample. Fortunately, however, the short wavelength region of the spectrum appearing on the plate, *i.e.*, the region below 2500Å or so, is not very rich in the spectral lines. On carefully examining this part of the plate lines belonging to the different elements are found which are good enough for the spectro-chemical analysis. For quite a few of the elements there are several lines available, some of which are more or less contaminated by the proximity of the lines belonging to the rest of the ele-



Percentage of N

FIG. 3

ments. The particular lines selected should thoroughly be scrutinized with the help of a good wavelength table for all possible contaminations and their magnitudes. Above all, photometric measurements should be carried out on a large number of plates to find out the effects, if any, produced by the contaminating elements; variable percentages of these elements should, of course, be contained in the samples used for producing the spectra. A preliminary survey has been carried out in the way indicated above. The cali-

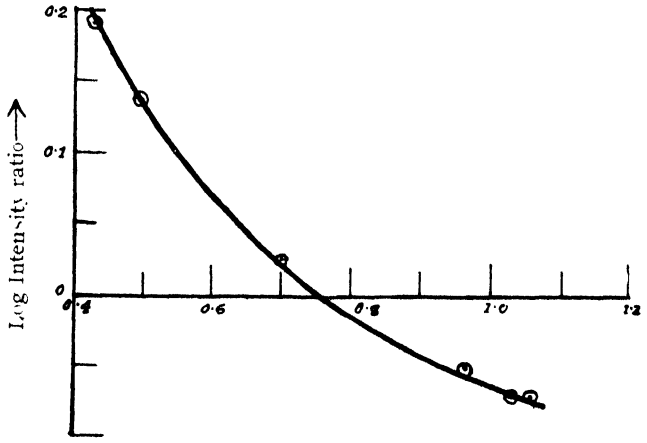


FIG. 4

bration curves for the quantitative determinations of some the elements mentioned are given below. They are very smooth and the results obtained in the few cases tried, check up well with the chemical values. There are, therefore good possibilities for using the medium spectrograph for the quantitative analysis of the ferrous alloys. More work will, however, be necessary to select the most suitable lines for the respective elements and it is being continued.

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